

Report on **Selenium Process Testing**

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This report presents the results of a study conducted for the Federal-State Interagency San Joaquin Valley Drainage Program. The purpose of the report is to provide the Drainage Program agencies with information for consideration in developing alternatives for agricultural drainage water management. Publication of any findings or recommendations in this report should not be construed as representing the concurrence of the Program agencies. Also, mention of trade names or commercial products does not constitute agency endorsement or recommendation.

The San Joaquin Valley Drainage Program was established in mid-1984 as a cooperative effort of the U.S. Bureau of Reclamation, U.S. Fish and Wildlife Service, U.S. Geological Survey, California Department of Fish and Game, and California Department of Water Resources. The purposes of the Program are to investigate the problems associated with the drainage of irrigated agricultural lands in the San Joaquin Valley and to formulate, evaluate, and recommend alternatives for the immediate and long-term management of those problems. Consistent with these purposes, Program objectives address the following key areas: (1) Public health, (2) surface- and ground-water resources, (3) agricultural productivity, and (4) fish and wildlife resources.

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**Selenium Process Testing
Report**

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1 CONCLUSIONS

1. The ferrous hydroxide method for reducing and removing selenate removed 56% of the selenate. These values were lower than expected, but were probably due to oxygen being dissolved in the test solution. This test was used to verify that the experimental and analytical procedures would catch the removal of selenate.
2. Thiourea and sulfuric acid removed 66% of the selenate.
3. Thiourea, sulfuric acid, and sulfur dioxide removed 91% of the selenate. Further work should be done to determine if it is possible to economically optimize this process.
4. ISX (Insoluble Starch Xanthate) removed 15% of the selenate. This process is not known to be able to remove low levels of selenium especially in the selenate state. Further work could be done, but the method does not look promising.
5. Iron sulfide (powdered iron pyrite) removed 23.8% of the selenate. Further work could be done to try to optimize selenate removal.
6. Sodium thiosulfate removed 10.3% of the selenate. Further work could be done to verify that selenium removal actually occurred and try to increase the amount of selenium removal.
7. "CYC" from Iso-Clear Systems Corporation removed 8.3% of the selenate. Further work could be done if "CYC" is different from ISX.
8. The Sulfex Process (Insoluble Sulfide Precipitation Process) did not remove any selenate.
9. The Soluble Sulfide Precipitation Process did not remove any selenate.
10. Hydrazine, using X-154 (sodium tri thio carbonate) from Iso-Clear Systems Corporation to form an insoluble sulfide after selenate reduction, did not remove any selenate.

2 INTRODUCTION

The Bureau of Reclamation's Division of Research and Laboratory Services, in Denver sent a proposal November 17, 1986 to the Regional Director of the Mid Pacific Region outlining costs to do bench-scale process evaluation, screening, and some process optimization for selenium removal from San Luis Drain water. This proposal was accepted by the Manager, San Joaquin Valley Drainage Program, Sacramento, CA, and Ed Lee visited the Denver Office from December 15-17, 1986. He met with various people including Ed Backstrom, Andy Murphy, Charles Moody, Roy Eisenhauer, and Lorentz Haugseth of the Chemistry,

Petrography, and Chemical Engineering Section. It was decided that six different chemicals were to be screened in bench-scale testing. They were: thiourea, sulfur dioxide, cellulose xanthate, hydrogen sulfide, sodium thiosulfate, and hydrazine sulfate. The actual processes tested were: ferrous hydroxide, thiourea, sulfur dioxide, cellulose xanthate (ISX), iron sulfide, sodium thiosulfate, "CYC", insoluble sulfide precipitation, soluble sulfide precipitation, and hydrazine sulfate with X-154.

This report describes the screening tests done for the San Joaquin Valley Drainage Program, and also briefly describes earlier work, in section 5.1.3 Tests That Did Not Work, done by Andy Murphy on an electron exchange resin.

3 PROCEDURES

3.1 Test Solution Makeup

The following tables describe how the test solution for the screening experiments was made. Table 1 shows the inorganic chemical constituents of the San Luis Drain. These were the target values used in modeling the test solution and came from the Department of Water Resources for the State of California. Two assumptions were made in order to use the information in the enclosure. First, San Luis Drain TDS was assumed to be 10,000 mg/L, and second, any trace element 20 $\mu\text{g}/\text{L}$ or less was not included in the test solution.

Table 2 shows the amount of chemicals added to make the synthetic San Luis Drain water. Note that unlike the previous table, this table has increased the selenium concentration to 20 mg/L in the selenate form in order to use flame AA to measure selenium concentrations.

Table 3 was used to check to see how closely the synthetic water would be to the original San Luis Drain water in Table 1. The only constituent in excess other than selenate was sulfate by 217 mg/L or approximately 5% more than in the actual water.

Constituent	mg/L	$\mu\text{g}/\text{L}$	MW	moles/L	valence	equiv/L
Ca ⁺²	500		40.08	1.25E-02	2	2.50E-02
Mg ⁺²	300		24.31	1.23E-02	2	2.47E-02
Na ⁺¹	2500		22.99	1.09E-01	1	1.09E-01
K ⁺¹	5		39.10	1.28E-04	1	1.28E-04
HCO ₃ ⁻¹	300		61.01	4.92E-03	-1	-4.92E-03
SO ₄ ⁻²	4300		96.06	4.48E-02	-2	-8.95E-02
Cl ⁻¹	2000		35.45	5.64E-02	-1	-5.64E-02
NO ₃ -N	30		14.01	2.14E-03	-2	-4.28E-03
PO ₄ -P	0.3		30.97	9.69E-06	-3	-2.91E-05
B ⁺³	13000		10.81	1.20E-03	3	3.61E-03
Cr ⁺³	35		52.00	6.73E-07	3	2.02E-06
Fe ⁺³	100		55.85	1.79E-06	3	5.37E-06
Mo ⁺⁶	75		95.94	7.82E-07	6	4.69E-06
Se ⁺⁶	350		78.96	4.43E-06	6	2.66E-05
Sr ⁺²	6400		87.62	7.30E-05	2	1.46E-04
				Total		6.98E-03

Table 1. - Original San Luis Drain composition to be modeled. (MW - molecular weight, equiv - equivalents)

Chemical	Unique Ion	g/L	g/100L	MW	moles/L
K ₂ SO ₄		1.11E-02	1.108	174.27	6.36E-05
Na ₂ SeO ₄	Se	4.78E-02	4.785	188.90	2.53E-04
Na ₂ B ₄ O ₇ ·10H ₂ O	B	1.15E-01	11.466	381.40	3.01E-04
SrCl ₂ ·6H ₂ O	Sr	1.95E-02	1.948	266.64	7.30E-05
Na ₂ MoO ₄ ·2H ₂ O	Mo	1.89E-04	0.019	241.98	7.82E-07
NaNO ₃	NO ₃	1.82E-01	18.203	84.99	2.14E-03
NaHCO ₃	HCO ₃	4.13E-01	41.310	84.01	4.92E-03
Na ₂ HPO ₄	PO ₄	1.37E-03	0.137	141.96	9.69E-06
Na ₂ SO ₄		4.92E+00	491.639	142.00	3.46E-02
MgSO ₄	Mg	1.49E+00	148.532	120.37	1.23E-02
K ₂ Cr ₂ (SO ₄) ₄ ·24H ₂ O	Cr	3.36E-04	0.034	998.40	3.37E-07
FeCl ₃ ·6H ₂ O	Fe	4.84E-04	0.048	270.32	1.79E-06
NaCl		1.83E+00	182.991	58.44	3.13E-02
CaCl ₂	Ca	1.77E+00	177.192	142.04	1.25E-02

Table 2. - Chemicals to be used to make San Luis Drain water.

Ion	MW	mg/L	$\mu\text{g/L}$	actual	desired	Difference
				moles/L	amount	moles/L
Ca ⁺²	40.08	500.0		1.25E-02	1.25E-02	0.00E+00
Mg ⁺²	24.31	300.0		1.23E-02	1.23E-02	0.00E+00
Na ⁺¹	22.99	2500.0		1.09E-01	1.09E-01	0.00E+00
K ⁺¹	39.10	5.0		1.28E-04	1.28E-04	0.00E+00
HCO ₃ ⁻¹	61.01	300.0		4.92E-03	4.92E-03	0.00E+00
SO ₄ ⁻²	96.06	4517.4		4.70E-02	4.48E-02	2.26E-03
Cl ⁻¹	35.45	2000.0		5.64E-02	5.64E-02	0.00E+00
NO ₃ -N	14.01	30.0		2.14E-03	2.14E-03	0.00E+00
PO ₄ -P	30.97	0.3		9.69E-06	9.69E-06	0.00E+00
B ⁺³	10.81		13000	1.20E-03	1.20E-03	0.00E+00
Cr ⁺³	52.00		35	6.73E-07	6.73E-07	0.00E+00
Fe ⁺³	55.85		100	1.79E-06	1.79E-06	0.00E+00
Mo ⁺⁶	95.94		75	7.82E-07	7.82E-07	0.00E+00
Se ⁺⁶	78.96		20000	2.53E-04	2.53E-04	0.00E+00
Sr ⁺²	87.62		6400	7.30E-05	7.30E-05	0.00E+00

Table 3. - Comparison of actual to artificial drain water constituents.

3.2 Analytical Methods

The chemical analysis of selenium, in any oxidation state, was performed on a Varian AA-975 using a nitrous oxide-acetylene flame. This method was chosen after much discussion, since the hydride method was known to be prone to interferences. Each new reduction method tested would have caused much additional expense and time in methods development to determine where interferences were coming from and ways to overcome the interferences. The nitrous oxide-acetylene method overcame those interferences.

Unfortunately, the use of the nitrous oxide-acetylene method has the major drawback of reducing the sensitivity of the analysis. The absolute minimum level of detection was calculated to be .8 mg/L selenium which was greater than the concentration reported in the San Luis Drain. All the screening experiments used a synthetic San Luis Drain water with 20 mg/L of selenium in the selenate form.

Table 4 shows the quality control calculations from the analysis of each set of tests. Note that the quality control methods changed from the beginning to end. By the end of the testing, the chemical analyses consisted of a blank of 0, and standards at 10, 20, 30 and 60 mg/L Se. Each sample measurement consisted of a blank, a 10 mg/L selenate spike (C), the sample (B), and the sample plus a 10 mg/L selenate spike (A), which were then used to calculate percent recovery. All the percent recoveries were within an acceptable range.

Percent recovery was calculated by the following equation:

$$\% \text{ recovery} = 100 \frac{A}{B+C}$$

A is defined as the spiked sample value.

B is defined as the sample value.

C is defined as the selenate spike value.

Test	Sample, mg/L Se (B)	Sample Plus Spike, mg/L Se (A)	Selenate Spike, mg/L Se (C)	Percent Recovery	Percent Recovery - 100
ISP pH 11 (average of 4)	20.2	N/A	N/A	N/A	N/A
ISP pH 8.5 (average of 4)	19.6	N/A	N/A	N/A	N/A
SSP pH 11 (average of 4)	19.0	N/A	N/A	N/A	N/A
Test solution (average of 3)	18.4	N/A	N/A	N/A	N/A
Hydrazine pH 8	21.6	32.5	8.8	107	7
ISX pH 3.1	18.1	25.0	9.7	90	-10
Ferrous Hydroxide pH 8.9	16.4	26.0	7.9	107	7
Ferrous Hydroxide pH 8.9	9.4	20.6	9.1	111	11
Test Solution	21.3	29.1	8.8	97	-3
FeS pH 8	17.7	24.2	5	107	7
FeS pH 9	17.0	22.3	5	101	1
Thiourea + H ₂ SO ₄	7.6	12.7	5	101	1
Thiourea	23.2	27.4	5	97	-3
Test Solution	22.3	26.1	5	96	-4
Na ₂ S ₂ O ₃ pH 2	21.9	27.4	5	102	2
Na ₂ S ₂ O ₃ pH 4	21.3	25.5	5	97	-3
Na ₂ S ₂ O ₃ pH 6	20.0	26.5	5	106	6
Na ₂ S ₂ O ₃ pH 8	20.3	26.1	5	103	3
Na ₂ S ₂ O ₃ pH 10	21.3	25.5	5	97	-3
80g H ₂ SO ₄ +SO ₂ +lg thiourea	2.3	13.2	10.0	100	8
8g H ₂ SO ₄ +SO ₂ +lg thiourea	9.0	20.4	10.3	105	5
80g H ₂ SO ₄ +SO ₂ +20mg thiourea	8.1	18.8	10.0	104	4
8g H ₂ SO ₄ +SO ₂ +20mg thiourea	23.5	35.6	11.0	103	3
Test Solution	24.3	35.6	10.0	104	4
CYC	20.0	28.5	10.3	94	-6
Test Solution	21.8	31.9	10.8	98	-2

Table 4. - Summary of analytical quality control. (ISP - insoluble sulfide process, SSP - soluble sulfide process)

3.3 Equipment Description

All of the experiments were conducted in a hood using a Phipps & Bird Stirrer, Model 7790-400 with stainless steel stirrers and plexiglass 2.5 L

square jar test containers. A model 601A Orion digital ionalyzer and a model 8102 Ross Electrode were used to measure pH. After the reactions had occurred, the samples were filtered through a Millipore model HAWP 04700, HA .45 um filter using a Nalgene, model 300-4050, 250 mL filter holder with receiver. The filtrate was placed into a 500 mL polyethelyene container until analysis.

3.4 Screening Tests

Appendices A through F describe the procedures used in the testing of each reduction method. The appendices also discuss the results, conclusions, and give a list of the articles that supported each method as a potential way to reduce selenate.

There were five sets of screening tests. These tests were done as chemicals came from the vendors. As the tests progressed the procedures and analytical methods improved. The results from these screenings can be seen in Table 5 in the next section.

4 RESULTS

The following table summarizes the results of each test in terms of the percent reduction and the relative significance of the reduction observed. Percent reduction was the amount of selenium removed by filtration due to precipitation or the creation of elemental selenium particles larger than .25 um. The significance column is a relative measure that divides one standard deviation of the percent recovery minus 100, of all the tests, into the percent reduction. (The values of percent recovery minus 100 can be found in Table 4.) Plus signs show that removal occurred, a period shows that a change in selenium concentration was less than one standard deviation, and a minus sign shows that the remaining selenium was greater than that originally present (due to analytical and/or experimental error).

Test	% Reduction	Significance Se
ISP pH 11 (average of 4)	-10.1	--
ISP pH 8.5 (average of 4)	-6.9	-
SSP pH 11 (average of 4)	-3.3	.
Test solution (average of 3)	0.0	.
Hydrazine pH 8	-1.4	.
ISX pH 3.1	15.0	++
Ferrous Hydroxide pH 8.9	23.0	++++
Ferrous Hydroxide pH 8.9	55.9	+++++++++
Test Solution	0.0	.
FeS pH 8	20.6	++++
FeS pH 9	23.8	++++
Thiourea + H ₂ SO ₄	65.9	+++++++++++++
Thiourea	-4.0	.
Test Solution	0.0	.
Na ₂ S ₂ O ₃ pH 2	1.8	.
Na ₂ S ₂ O ₃ pH 4	4.5	.
Na ₂ S ₂ O ₃ pH 6	10.3	++
Na ₂ S ₂ O ₃ pH 8	9.0	+
Na ₂ S ₂ O ₃ pH 10	4.5	.
80g H ₂ SO ₄ +SO ₂ +lg thiourea	90.7	+++++++++++++
8g H ₂ SO ₄ +SO ₂ +lg thiourea	62.8	+++++++
80g H ₂ SO ₄ +SO ₂ +20mg thiourea	66.7	+++++++
8g H ₂ SO ₄ +SO ₂ +20mg thiourea	2.9	.
Test Solution	0.0	.
CYC	8.3	+
Test Solution	0.0	.

Table 5. - Test results.

5 DISCUSSION

This section will discuss the results of the screening tests in terms of those that worked, those that could use further study, and those that did not work. Also, there is a discussion of the compromises in the experimental design that was used in the screening experiments.

5.1 Discussion of Results

5.1.1 Tests That Worked

Three selenate reduction methods worked. Ferrous hydroxide (the method being developed by Andy Murphy and Charles Moody of the Denver Office) which was not included in the original list of chemicals to be screened, achieved about a 56% removal of selenate. The second method was thiourea and sulfuric acid with a 66% removal of selenate. The third method was thiourea, sulfuric acid, and sulfur dioxide with approximately a 91% removal (see Table 5).

The ferrous hydroxide method is being extensively studied by the Chemistry, Petrography, and Chemical Engineering Section at the USBR's Denver Office. Much better results than those seen in this report have been attained in distilled water and in actual San Luis Drain water, because no effort was made during these tests to keep oxygen away from the reaction. This test was included in the screening in order to verify that the experimental and analytical procedures would actually catch the removal of selenium. This test also indicated that dissolved oxygen from the atmosphere did not totally interfere with the reduction of selenate.

Selenium reduction and removal was also achieved using a combination of thiourea, sulfuric acid, and sulfur dioxide. Note that thiourea alone did not remove any of the selenate. A very simple optimizing experimental design, a two-level two-factor design, was performed by varying the amount of sulfuric acid and thiourea. The amounts of selenium removed in the four tests ranged from 2.9% all the way to 90.7%. Unfortunately, the best removal occurred at the highest levels of sulfuric acid and thiourea, which could make this an uneconomic method for selenium removal. Further designed experiments might find a region that minimizes the amount of reactants required and still removes the majority of the selenium.

5.1.2 Tests That Could Use Further Study

Four selenate reduction and removal methods were partially successful, which may be due to testing at the wrong conditions or experimental error. ISX (Insoluble Starch Xanthate) showed a 15% removal, iron sulfide (iron pyrite) removed 23.8%, sodium thiosulfate removed 10.3%, and "CYC" appeared to remove 8.3% (see Table 5).

ISX was a very simple reaction, but in talking to the inventor of the method it was found that the ISX process doesn't work well with low levels of selenium. Further work with ISX could be done, although it does not look promising.

Sodium thiosulfate appeared to remove some of the selenate at a pH of 6. Further work could be done to see if removal actually occurred. Also, work could be done to optimize the removal by varying the pH in small increments around pH 6, increasing the temperature, or increasing the concentration of the thiosulfate.

Iron sulfide in the form of an iron pyrite powder did remove some of the selenate. Further work could be done to optimize the process by varying the pH, temperature, concentration of the sulfide, and concentration of the selenate. One problem noticed with this process was that as oxygen diffused into the solution large amounts of iron oxide were formed.

"CYC", which appears to be an insoluble starch xanthate bead, was another simple reaction. This reactant was tested at the very last of the screening and should have more investigation, especially if it is different from ISX.

5.1.3 Tests That Did Not Work

The Sulfex Process or Insoluble Sulfide Precipitation Process did not remove any of the selenate. The Soluble Sulfide Precipitation Process did not remove any of the selenate. The hydrazine used with X-154 (sodium tri thio carbonate) to form an insoluble sulfide also did not remove any of the selenate (see Table 5).

5.1.3.1 Electron Exchange Resin

In 1985 and 1986 several reports were written by Andy Murphy, Bureau of Reclamation Chemist, concerning the removal of selenium by an electron exchange resin. These reports are USBR, Division of Research and Laboratory Services, Applied Sciences Memoranda 85-3-2, 85-3-8, and 85-3-10. Initially, the results indicated that selenate

and selenite were being reduced by the transfer of electrons from a hydroquinone functional group regenerated with sodium hydrosulfite. Upon further study with new resin and new sodium selenate it was discovered that the electron exchange resin was acting as an ion exchange resin and that the previous sodium selenate had been contaminated by selenium metal. Even though the selenate and selenite were removed by an ion exchange process, sulfate interfered with the selenium removal.

5.2 Discussion of Experimental Design

There were many compromises in the design of the experiments detailed in this report. Foremost among these was the use of 20 mg/L selenium in the form of selenate. Others included the use of selenate rather than a mixture of selenate and selenite, synthetic water vs. actual San Luis Drain water, not always testing at various pH levels, and one reactant rather a full class of reactants.

The procedures section of the report explained that 20 mg/L selenium in the form of selenate was used so that the measurement of selenium removal would have no interferences. Ideally, reduction of San Luis Drain water with approximately 350 $\mu\text{g}/\text{L}$ of selenium as selenate and selenite would have been tested, but some control over what would be reduced was necessary. Therefore, only selenate was added to the test solution, and the tests only indicate how much selenate was removed. Note that every process can remove selenite to some degree, see references at the end of each appendix.

Choices in the correct pH, temperature, reaction time, and proper reactant were made based upon articles in the selenium literature. In some cases, a screen on one variable such as pH was made, but in general, conditions were those suggested by a vendor or from reports in the literature. All the processes were adjusted for 20 mg/L selenium, and when the information was available the reactants were in considerable excess over the stoichiometric amount needed to reduce the selenate.

6 APPENDIX A - Sulfur Dioxide & Thiourea

6.1 Sulfur Dioxide and Thiourea

The purpose of the test was to determine if sulfur and thiourea would remove selenium in the selenate form from a synthetic San Luis Drain water. This test was the only series of experiments that was experimentally designed to help in optimizing the process.

6.1.1 Procedure

The procedures that were used in the tests are listed below.

1. Mix the salts into a covered 50 L polyethylene tank to make synthetic San Luis Drain water. The recipe follows:

Potassium Sulfate	.554 grams
Sodium Selenate	2.392 grams
Sodium Borate 10 Hydrate	5.733 grams
Strontium Chloride 6 Hydrate	.974 grams
Sodium Molibdate 2 Hydrate	.010 grams
Sodium Nitrate	9.102 grams
Sodium Bicarbonate	20.655 grams
Sodium Hydrogen Phosphate	.069 grams
Sodium Sulfate	245.819 grams
Magnesium Sulfate	74.266 grams
Potassium Chromium	.017 grams
Sulfate 24 Hydrate	
Ferric Chloride 6 Hydrate	.024 grams
Sodium Chloride	91.496 grams
Calcium Chloride	88.596 grams

NOTES:

Selenium concentration was approximately 20 mg/L
 Salts were dissolved in 2L beakers using magnetic stirring bars and heat if necessary. The solution used to dissolve the salts came from the 50 L container, originally containing deionized water.

When each salt was dissolved, the resulting solution was poured back into the 50 L container.

A small mixer was used to mix the 50 L solution while the salt solutions were poured in and when any solution was used for testing.

When the small mixer was not in use the 50 L tank was covered.

pH was adjusted to 7.2.

2. The rotometer was calibrated using compressed air.

3. Two liters of the salt solution were transferred to each of the four square mixing tanks.
4. The square tanks were placed on the Phipps and Bird jar test apparatus.
5. The jar test apparatus was set for 100 rpm for two hours.
6. Sulfur dioxide flow was set at 3, which corresponded to 81.6 mL of gas per minute.
7. 80 grams, 8 grams, 80 grams, and 8 grams of concentrated sulfuric acid were added to tanks #1, #2, #3, and #4. After five minutes, 1 gram, 1 gram, 20 milligrams, and 20 milligrams of thiourea were added to tanks #1, #2, #3, and #4.
8. A Nalgene filter holder and receiver using .45 um Millipore filters were prepared for each sample.
9. The contents were filtered, then the 250 mL of filtrate were placed into a labeled polyethylene container. This was repeated for each sample.
10. All the samples were analyzed using a nitrous oxide-acetylene flame AA instrument with recoveries, spike, and blank done with each sample.

In summary, the tests were as follows:

Test 1 - 80 g H₂SO₄, 1 g thiourea
Test 2 - 8 g H₂SO₄, 1 g thiourea
Test 3 - 80 g H₂SO₄, 20 mg thiourea
Test 4 - 8 g H₂SO₄, 20 mg thiourea

6.1.2 Results

The synthetic San Luis Drain solution was determined to have 24.3 mg/L selenium, while tests #1, 2, 3, and 4 had 2.3, 9.0, 8.1, and 23.5 mg/L of selenium respectively.

Note that the samples were analyzed three months after the tests, since the first analyses were done with a failing lamp. Any selenium that might have precipitated should have been shaken back into the solution and measured by the AA.

6.1.3 Conclusion

Tests #1, 2, 3, 4 removed 90.7%, 62.8%, 66.7%, and 2.9% of the selenium in the synthetic water. The highest removal occurred with the

highest levels of the reactants. The sulfur dioxide concentrations were not varied, since the amount of sulfur dioxide that dissolved into solution could not be measured.

6.2 Thiourea

The purpose of the test was to determine if thiourea alone would remove selenium in the selenate form from a synthetic San Luis Drain water.

6.2.1 Procedure

See Appendix A section 1.1 for the procedure used in making the synthetic San Luis Drain water.

1. Two liters of the salt solution were transferred to two of the square mixing tanks.
2. The square tanks were placed on the Phipps and Bird jar test apparatus.
3. The jar test apparatus was set for 100 rpm for approximately four hours.
4. 1.93 grams of thiourea were added to tanks #1 and #2 for 50 times the stoichiometric concentration of selenium.
5. To tank #1, 80 grams of concentrated sulfuric acid were added.
6. A Nalgene filter holder and receiver using .45 um Millipore filters were prepared for each sample.
7. The contents were filtered, then the 250 mL of filtrate were placed into a labeled polyethylene container. This was repeated for each sample.
8. All the samples were analyzed using a nitrous oxide-acetylene flame AA instrument.

In summary, the tests were as follows:

Test 1 - 80 g H₂SO₄, 1.93 g thiourea

Test 2 - 1.93 g thiourea

6.2.2 Results

The synthetic San Luis Drain water had 22.3 mg/L selenium, but after reacting the synthetic water with thiourea and sulfuric acid only 7.6 mg/L selenium remained. When the same solution was reacted with only thiourea, 23.2 mg/L selenium remained.

6.2.3 Conclusion

The selenium concentration of the thiourea and concentrated sulfuric acid decreased from 22.3 mg/L in the test solution to 7.6 mg/L after the test. There was approximately a 65.9% removal of selenium. The selenium concentration of the thiourea increased from 22.3 mg/L in the test solution to 23.2 mg/L after the test. Most likely, the increase in selenium was due to error in the analytical methods.

6.3 Articles

"Selenium", ed. R.A. Zingaro and W.C. Cooper, 1974, pp. 57-8, 60-1, 109.

U.S. Patent 2,834,652, May 13, 1958. "Recovery of Selenate Values Contained in Sulfuric Acid Solutions", M.L. Hollander and Y.E. Lebedeff.

7 APPENDIX B - Cellulose Xanthate (Insoluble Starch Xanthate)

The purpose of the test was to determine if cellulose xanthate (insoluble starch xanthate) would remove selenium in the selenate form from a synthetic San Luis Drain water.

7.1 Procedure

See Appendix A for the procedure used in making the synthetic San Luis Drain water.

1. The pH meter was calibrated using a pH 4 buffer.
2. Two liters of the salt solution were transferred to one square mixing tanks.
3. The square tank was placed on the Phipps and Bird jar test apparatus.
4. The jar test apparatus was set for 100 rpm for approximately one hour.
5. The pH of the reactor was adjusted to 3.1 using HCl.
6. 60 grams of insoluble starch xanthate were added to the tank for greater than 40 times the ratio of ISX to selenium used by R.E. Wing in his 1979 article.
7. pH was continuously adjusted during the test.
8. A Nalgene filter holder and receiver using .45 um Millipore filters were prepared.
9. The test solution was filtered, then the 250 mL of filtrate was placed into a labeled polyethylene container.
10. The sample was analyzed using a nitrous oxide-acetylene flame AA instrument.

7.2 Results

There was 18.1 mg/L Se remaining after the test.

7.3 Conclusion

The selenium concentration decreased from 21.3 mg/L in the test solution to 18.1 mg/L after the test. There was approximately a 15% decrease in selenium.

7.4 Articles

"Selenium", ed. R.A. Zingaro and W.C. Cooper, 1974, pp. 37.
Product literature from Stout's Supply, RR #1, Ainsworth, IA 52201,
(319) 657-4127.
Product technical data sheet from Stout's Supply, RR #1, Ainsworth, IA
52201, (319) 657-4127.

"Insoluble Starch Xanthate: Preparation, Stabilization, Scaleup and Use", R.E. Wing, B.K. Jasberg, and L.L. Navickis, *Starch/Starke* 30 (1978), No. 5, pp. 163-170.

"Solvent Extraction of Metal Xanthates", E.M. Donaldson, *Talanta*, Vol. 23, 1976, pp. 417-426.

"Corn Starch Compound Recovers Metals From Water", R.E. Wing, *Industrial Wastes*, Jan/Feb, 1975, pp. 26-27.

"ISX Reduces Selenium Count In Process Wastewaters", L.L. Navickis, R.E. Wing, and E.B. Bagley, *Industrial Wastes*, Jan/Feb, 1979, pp. 26-30.

"Dissolved Heavy-Metal Removal by Insoluble Starch Xanthate (ISX)", R.E. Wing, *Environmental Progress*, Vol. 2, No. 4, Nov., 1983, pp. 269-272.

"Electroplating Wastewater Pollution Control Technology", pp. 130-136, source unknown.

"Starch-based Products Effective In Heavy Metal Removal", R.E. Wing, W.E. Rayford, *Proceedings 31st Industrial Waste Conference*, Purdue Univ., W. Lafayette, Indiana (May 4-6, 1976), 1977, pp. 1068-1079.

"Environmental II Session S, Case History Reports On Heavy Metal Removal Process", "Ann. Tech. Conf. Am. Electroplat Soc.", 66th R.E. Wing, Atlanta, Ga., June 24 1979, Publ. by Am. Electroplat. Soc., Winter Park Fla., 1979, Pap. S-3, pp. 1-39.

"Insoluble Starch Xanthate: Use in Heavy Metal Removal", R.E. Wing, W.M. Doane, and C.R. Russell, *Journal of Applied Polymer Science*, Vol. 19, pp. 847-854, 1975.

"Starch purifies PC rinse waters", R.E. Wing, *Circuits Manufacturing* (1976), 16(12):10,12,14-16.

8 APPENDIX C - Metal Sulfides (Hydrogen Sulfide)

Three different processes were tested for selenium removal by using metal sulfides. They were: iron sulfide in the form of iron pyrite, the insoluble sulfide precipitation process (ISP), and the soluble sulfide precipitation process (SSP).

8.1 Iron Pyrite

The purpose of the test was to determine if iron pyrite would remove selenium in the selenate form from a synthetic San Luis Drain water. Note that the first set of tests was not reported due to poor analytical quality control.

8.1.1 Procedure

See Appendix A for the procedure used in making the synthetic San Luis Drain water. The remaining procedures are listed below.

1. Two liters of the salt solution were transferred to each of two of the square mixing tanks.
2. Oxygen was purged from each tank overnight with nitrogen. The nitrogen purge continued through the experiments.
3. The pH meter was calibrated using buffers of pH 7 and 10.
4. Fifty grams of iron sulfide powder were added to each tank. The powder was ground iron pyrite that had been passed through a No. 16 screen (.0469 inches).
5. The pH of one tank was adjusted to 8, and the other tank was adjusted to 9.
6. Each tank was placed on the Phipps and Bird jar test apparatus with the stirring speed set for 200 rpm. The test was run overnight, for approximately a 23-hour reaction time.
7. A Nalgene filter holder and receiver using .45 um Millipore filters were prepared for each sample.
8. The contents were filtered, then the 250 mL of filtrate was placed into a labeled polyethylene container. This was repeated for each sample.
9. Each sample was acidified by adding 10 drops of concentrated HCl to prevent precipitation of iron hydroxide.
10. All the samples were analyzed using a nitrous oxide-acetylene flame AA instrument.

In summary, the tests were as follows:

- Test 1 - pH 8, iron sulfide powder
- Test 2 - pH 9, iron sulfide powder

8.1.2 Results

AA analysis showed that 17.7 mg/L selenium remained at pH 8, and 17.0 mg/L selenium remained at pH 9. The test solution before treatment showed 22.3 mg/L selenium.

8.1.3 Conclusion

Iron sulfide showed a removal of 20.6% of selenium at a pH of 8, and a removal of 23.8% of selenium at a pH of 9.

8.2 ISP and SSP

The purpose of the test was to determine if the insoluble sulfide precipitation process or the soluble sulfide precipitation process would remove selenium in the selenate form from a synthetic San Luis Drain water.

8.2.1 Procedure

See Appendix A for the procedure used in making the synthetic San Luis Drain water. The remaining procedures are listed below.

1. The pH meter was calibrated using buffers of pH 10 and 12.45.
2. Two liters of the salt solution were transferred to each of the five square mixing tanks.
3. The square tanks were placed on the Phipps and Bird jar test apparatus.
4. The jar test apparatus was set for 90 rpm for a minimum of five hours.
5. The pH of tanks #1,2,3,4, and 5 was adjusted to pH 11 by adding 2.5 N NaOH.
6. 1.406 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.284 g of NaHS were added to tanks #1, #2, #3, and #4 for 10 times the stoichiometric concentration of selenium.
7. pH was monitored hourly and adjusted if necessary.
8. The contents of each square mixing tank was moved to its own covered 2 L beaker and let settle overnight.
9. A Nalgene filter holder and receiver using .45 um Millipore filters were prepared for each sample.

10. Each sample was acidified by adding 5 drops of concentrated HCl to prevent precipitation of iron hydroxide.
11. The contents were filtered, then the 250 mL of filtrate was placed into a labeled polyethylene container. This was repeated for each sample.
12. The pH meter was recalibrated using buffers of pH 7 and 10.
13. Two liters of the salt solution were transferred to each of the five square mixing tanks.
14. The square tanks were placed on the Phipps and Bird jar test apparatus.
15. The jar test apparatus was set for 90 rpm for a minimum of 5 hours.
16. $\text{Ca}(\text{OH})_2$ was added to tanks #6,7,8,9, and 10 until the pH reached 8.5, then 0.284 g of NaHS was added to tanks #6,7,8, and 9 for 10 times stoichiometric concentration.
17. Steps 7 through 11 were then repeated.
18. The pH meter was recalibrated using buffers of pH 10 and 12.45.
19. Two liters of the salt solution were transferred to each of the five square mixing tanks.
20. The square tanks were placed on the Phipps and Bird jar test apparatus.
21. The jar test apparatus was set for 90 rpm for a minimum of 5 hours.
22. $\text{Ca}(\text{OH})_2$ was added to tanks #6,7,8,9, and 10 until the pH reached 8.5, then 0.284 g of NaHS was added to tanks #6,7,8, and 9 for 10 times stoichiometric concentration.
23. Steps 7 through 11 were then repeated.
24. All the samples were analyzed using a nitrous oxide-acetylene flame AA instrument.

In summary, the tests were as follows:

First Set:

- Test 1 - pH 11, Insoluble Sulfide Process
- Test 2 - repeat of Test 1
- Test 3 - repeat of Test 1
- Test 4 - repeat of Test 1
- Test 5 - control, pH 11, no chemicals added to water

Second Set;

- Test 6 - pH 8.5, Insoluble Sulfide Process
- Test 7 - repeat of Test 6
- Test 8 - repeat of Test 6
- Test 9 - repeat of Test 6

Test 10 - control, pH 8.5, no chemicals added to water
 Third Set:

Test 11 - pH 11, Soluble Sulfide Process

Test 12 - repeat of Test 11

Test 13 - repeat of Test 11

Test 14 - repeat of Test 11

Test 15 - control, pH 11, no chemicals added to water

8.2.2 Results

Table 1C shows the selenium concentrations measured by nitrous oxide-acetylene flame.

Test	Description	Concentration, mg/L Se
Test #1	ISP, pH 11	19.64
Test #2	ISP, pH 11	21.82
Test #3	ISP, pH 11	19.64
Test #4	ISP, pH 11	19.64
Test #5	control, pH 11	18.23
Test #6	ISP, pH 8.5	18.23
Test #7	ISP, pH 8.5	22.19
Test #8	ISP, pH 8.5	19.84
Test #9	ISP, pH 8.5	18.23
Test #10	control, pH 8.5	19.64
Test #11	SSP, pH 11	20.00
Test #12	SSP, pH 11	20.72
Test #13	SSP, pH 11	18.93
Test #14	SSP, pH 11	16.18
Test #15	control, pH 11	17.19

Table 1C. - Test Results

8.2.3 Conclusion

No selenium removal occurred when using the two sulfide processes.

8.3 Articles

EPA Summary Report "Control and Treatment Technology for the Metal Finishing Industry, Sulfide Precipitation", April 1980, EPA 625/8-80-003.

"Separation of Toxic Heavy Metals by Sulfide Precipitation", D. Bhattacharyya, A.B. Jumawan, and R.B. Grieves, Separation Science and Technology, 14(5), pp. 441-452, 1979.

9 APPENDIX D - Sodium Thiosulfate

The purpose of the test was to determine if sodium thiosulfate would remove selenium in the selenate form from a synthetic San Luis Drain water.

9.1 Procedure

See Appendix A for the procedure used in making the synthetic San Luis Drain water.

1. The pH meter was calibrated using buffers of pH 4, 7, and 10, depending upon the pH of the test.
2. Two liters of the salt solution were transferred to each of the five square mixing tanks.
3. The square tanks were placed on the Phipps and Bird jar test apparatus.
4. The jar test apparatus was set for 200 rpm for approximately four hours.
5. 4 grams of $\text{Na}_2\text{S}_2\text{O}_3$ were added to tanks #1, #2, #3, and #4 for 50 times the stoichiometric concentration of selenium.
6. The pH of tanks #1,2,3,4, and 5 was adjusted to the proper pH using NaOH and HCl.
7. A Nalgene filter holder and receiver using .45 um Millipore filters were prepared for each sample.
9. The contents were filtered, then the 250 mL of filtrate was placed into a labeled polyethylene container. This was repeated for each sample.
10. All the samples were analyzed using a nitrous oxide-acetylene flame AA instrument.

In summary, the tests were as follows:

Test 1 - pH 2
Test 2 - pH 4
Test 3 - pH 6
Test 4 - pH 8
Test 5 - pH 10

9.2 Results

Table 1D shows the selenium concentrations measured by nitrous oxide-acetylene flame.

Test	Description	Concentration mg/L Se
Test #1	Na ₂ S ₂ O ₃ pH 2	21.9
Test #2	Na ₂ S ₂ O ₃ pH 4	21.3
Test #3	Na ₂ S ₂ O ₃ pH 6	20.0
Test #4	Na ₂ S ₂ O ₃ pH 8	20.3
Test #5	Na ₂ S ₂ O ₃ pH 10	21.3

Table 1D. - Test Results Using Na₂S₂O₃

9.3 Conclusion

The selenium concentration at pH 6 decreased from 22.3 mg/L in the test solution to 20.0 mg/L after the test. There was approximately a 10.3% removal of selenium. The removal decreased at all the other pH's.

9.4 Articles

USBR Translation of "Reaction of Selenate with Sodium Thiosulfate in Alkaline Solutions at Elevated Temperatures" from the Russian: Eksp. Issled. Kim. Biol., Karagand. Gos. Univ., Karaganda, USSR, pp. 81-83, 1974.

10 APPENDIX E - Hydrazine Sulfate

The purpose of the test was to determine if hydrazine sulfate would remove selenium in the selenate form from a synthetic San Luis Drain water. The first set of tests are not reported here, since they were done at very low concentrations of reactants.

10.1 Procedure

See Appendix A for the procedure used in making the synthetic San Luis Drain water.

1. The pH meter was calibrated using buffers of pH 7 and 10.
2. Two liters of the salt solution were transferred to one of the square mixing tanks.
3. The square tank was placed on the Phipps and Bird jar test apparatus.
4. The jar test apparatus was set for 90 rpm for three hours.
5. 120 grams of hydrazine sulfate were added to the tank to match the ratio of reactant to selenium used in previous work done by Iso-Clear Systems Corporation with 1 mg/L selenium solutions.
6. The pH of the tank was adjusted to 8 using NaOH.
7. After three hours 20 mL of 10% X-154 (sodium tri thio carbonate) was added to the reactor. This quantity also matched the ratio of reactant to selenium used in the previous work done by Iso-Clear.
8. A Nalgene filter holder and receiver using .45 um Millipore filters were prepared for each sample.
9. One hour after step 7. the contents were filtered, then the 250 mL of filtrate was placed into a labeled polyethylene container.
10. The sample was analyzed using a nitrous oxide-acetylene flame AA instrument.

10.2 Results

There was 21.6 mg/L Se remaining after the test.

10.3 Conclusion

The selenium concentration increased from 21.3 mg/L in the test solution to 21.6 mg/L after the test. There was approximately a 1.4% increase in selenium. Most likely, the increase in selenium was not real and was due to analytical error in measurement of the selenium values.

10.4 Process Source

Iso-Clear Systems Corporation, 208 Beaver Street, Yorkville, Illinois 60560, (312) 553-0671.

11 APPENDIX F - Other Processes

11.1 Ferrous Hydroxide

The purpose of the test was to determine if ferrous hydroxide would remove selenium in the selenate form from a synthetic San Luis Drain water.

11.1.1 Procedures

See Appendix A for the procedure used in making the synthetic San Luis Drain water.

1. The pH meter was calibrated using buffers at pH 7 and 10.
2. Two liters of the salt solution were transferred to two of the square mixing tanks.
3. The square tanks were placed on the Phipps and Bird jar test apparatus.
4. The jar test apparatus was set for 90 rpm for three hours.
5. In tank #1, 3.8 grams of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1.094 grams of NaOH were added. In tank #2 7.6 grams of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 2.188 grams of NaOH were added.
6. The pH of tanks #1 and 2 was adjusted to pH 8.9 by adding NaOH and HCl as necessary.
7. A Nalgene filter holder and receiver using .45 um Millipore filters were prepared for each sample.
8. The contents were filtered, then the 250 mL of filtrate was placed into a labeled polyethylene container. This was repeated for each sample.
9. The two samples were analyzed using a nitrous oxide-acetylene flame AA instrument.

In summary, the tests were as follows:

Test 1 - pH 8.9, 2.8 g/2L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 1.094 g/2L NaOH

Test 2 - pH 8.9, 7.6 g/2L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 2.188 g/2L NaOH

11.1.2 Results

The synthetic drain water before testing had 21.3 mg/L of selenium. After test #1 there was 16.4 mg/L selenium, and after test #2 there was 9.4 mg/L selenium.

11.1.3 Conclusions

Test #1 removed 23% of the selenium and test #2 removed 55.9%. These values were lower than expected, but were probably due to oxygen being dissolved in the test solution.

11.1.4 Articles

"Removal of Selenate from Water by Chemical Reduction", A.P. Murphy, Ind. Eng. Chem. Res. 1988, 27, 187-191.

11.2 CYC

The purpose of the test was to determine if "CYC" would remove selenium in the selenate form from a synthetic San Luis Drain water.

11.2.1 Procedures

See Appendix A for the procedure used in making the synthetic San Luis Drain water.

1. One liter of the salt solution was transferred to one of the square mixing tanks.
2. The square tank was placed on the Phipps and Bird jar test apparatus.
3. Two hundred mL of the beads were measured in a graduated cylinder and added to the square mixing tank. Before adding the beads to the test solution the water with the beads was decanted.
4. The jar test apparatus was set for 100 rpm for one hour.
5. A Nalgene filter holder and receiver using .45 um Millipore filters were prepared for the sample.
6. The contents were filtered, then the 250 mL of filtrate was placed into a labeled polyethylene container.
7. The sample was analyzed using a nitrous oxide-acetylene flame AA instrument.

11.2.2 Results

The synthetic drain water before testing had 21.8 mg/L of selenium. After the test there was 20.0 mg/L selenium

11.2.3 Conclusions

"CYC" removed approximately 8.3% of the selenium.

11.2.4 Process Source

Iso-Clear Systems Corporation, 1976 Oak Ridge Turnpike, Oak Ridge,
TN 37830, (615) 482-2563.

12 APPENDIX G - General Articles

"Metal removal by physical and chemical treatment processes", T. Maruyama, S.A. Hannah, and J.M. Cohen, Journal WPCF, Vol. 47, No. 5, May 1975, pp. 962-975.

"Removal of uncommon trace metals by physical and chemical treatment processes", S.A. Hannah, M. Jelus, J.M. Cohen, Journal WPCF, November 1977.

"Comparing chemical precipitation methods for water treatment", E.F. Bellew, Chemical Engineering, March 13, 1978, pp. 85-91.

"Mixing, Flocculation and Clarification", source unknown.

"Removal of toxic metals from power-generation waste streams by adsorption and coprecipitation", M.M. Benjamin, K.F. Hayes, J.O. Leckie, Journal WPCF, Vol. 54, No. 11, Nov. 1982, pp. 1472-1481.



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